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Carbon Support-Mediated Control of Selectivity for the Palladium-Catalyzed Hydrogenation of Multifunctional Chemicals

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Introduction

Carbon-supported noble metal catalysts are widely used for biomass conversion reactions due to the structural stability of carbon scaffolds under liquid phase reaction conditions. Although often considered as an inert support, the physico-chemical properties of carbon materials are known to impact the catalytic performance of the noble metal active phase. Currently, these differences in catalytic performance are attributed to metal-support interactions (MSI). However, the exact nature of the MSI still remains elusive [1,2]. This gap in understanding acts as a major barrier for the rational design of carbon supported catalysts.

Progress to address this barrier has been slow due to the heterogeneous nature of the carbon scaffolds at the nanoscale and the convolution of electronic and chemical effects that impact the metal active phase and the adsorption of reactants on the surface. The present study aimed at de-convoluting these effects by decreasing the level of structural complexity of the studied carbons. This approach provided unprecedented insights into MSI effects for carbons, in particular on their impact on selectivity.

Materials and Methods

Using chemical and thermal treatments, two independent series of support materials- i) with increasing degree of graphitization and ii) with increasing surface functionalization, were obtained. Pd nanoparticles were deposited on the supports by incipient wetness impregnation using Pd salts that decompose at low temperature. The activity of the catalysts was probed with the hydrogenation of cinnamaldehyde, an α,β -unsaturated aldehyde, under conditions that prevent the formation of palladium hydride and hydrogen spillover. Extensive catalyst characterization was conducted using X-ray diffraction (XRD), Raman spectroscopy, hydrogen adsorption isotherms, high pressure Fourier transform infrared spectroscopy, aberration corrected transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy using synchrotron radiation (XPS).

Results and Discussion

Clear trends in selectivity were observed with support graphitization and functionalization for C=C/C=O bond hydrogenation in multifunctional chemicals (Figure 1). The selectivities were compared under kinetically controlled regime at iso-conversion and

constant reaction time; similar turnover frequencies were obtained for all catalysts. Particle size effects were ruled out as TEM, XRD, and hydrogen chemisorption studies confirmed that all the catalysts presented 3-5 nm Pd nanoparticles, independent of the nature of the carbon support. Aberration corrected TEM confirmed that the metal interatomic distances are consistent with bulk Pd metal. Yet, the presence of a Pd^{δ+} phase was detected using synchrotron radiation XPS and the contribution of this phase was observed to increase with increasing support graphitization and decreasing functionalization. These correlations were consistent with changes observed for hydrogen chemisorption and selectivity to C=C bond hydrogenation. Further investigations revealed that alterations of the support through graphitization and functionalization impact its work function and thereby the metal-support charge transfers. DFT calculations further corroborated these MSI effects.

Significance

The correlations between the support properties and the MSI effects that have been established in this work are expected to set the foundations of more general rules for the rational design of carbon-supported catalysts for a broad range of reactions, beyond hydrogenations.

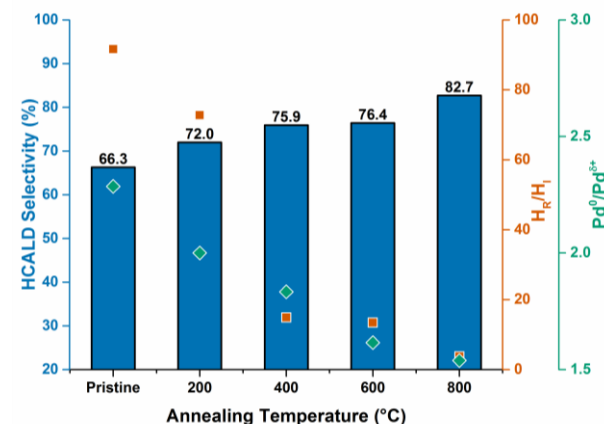


Figure 1. Selectivity towards hydrocinnamaldehyde (HCALD) at 10% conversion for Pd/C catalysts synthesized with carbon supports annealed at different temperatures; Ratio of the reversibly and irreversibly bound hydrogen from hydrogen chemisorption (H_R/H_I) ■ ; Ratio of the peak intensity for Pd in the metallic state to δ^+ charged state as observed with XPS using synchrotron radiation ($Pd^0/Pd^{\delta+}$) ◆.

References

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